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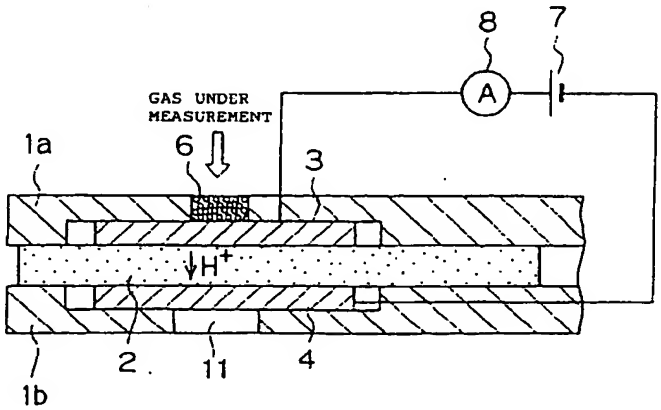
(54) Hydrogen gas sensor

(57) In a hydrogen gas sensor, the flow sectional area of a diffusion-rate limiting portion 6 is rendered small; the electrode surfaces of first and second electrodes 3 and 4 are rendered large; and/or a solution containing a polymer electrolyte identical with that of a proton-conductive layer 2 is applied onto the surfaces of the first and second electrodes 3 and 4 to thereby form a layer containing the polymer electrolyte. Thus, the rate of conduction of protons from the first electrode 3 to the second electrode 4 becomes greater than the rate at which protons are derived from hydrogen gas which is introduced onto the first electrode 3 via the diffusion-rate limiting portion 6. A hydrogen gas sensor capable of accurately measuring a hydrogen gas concentration of a measurement gas atmosphere in the presence of a variety of interfering gasses such as H_2O and CO is thereby provided.

Fig. 1



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Description

[0001] The present invention relates to a hydrogen gas sensor. and more particularly, to a hydrogen gas sensor suitable for measurement of hydrogen gas concentration of a fuel gas used for fuel cells.

[0002] In view of the issue of global-scale environmental deterioration, fuel cells, which are clean and efficient power sources, have recently become the subject of active studies. Among fuel cells, a polymer electrolyte fuel cell (PEFC) is expected to be suitable for vehicle use due to its advantages, including low operation temperature and high output density. In this case, a reformed gas obtained from methanol or the like is advantageously used as a fuel gas. Further, in order to improve efficiency and other parameters of performance, a gas sensor capable of directly measuring a hydrogen gas concentration of the reformed gas becomes necessary.

[0003] Since such a hydrogen gas sensor is used in a hydrogen-rich atmosphere, the operation temperature of the gas sensor must be low (about 100°C or less). Such a low-operation-temperature-type sensor is disclosed in Japanese Patent Publication *(kokoku)* No. 7-31153. In the sensor, a working electrode, a counter electrode, and a reference electrode are disposed on an insulating substrate, and the three electrodes are integrally covered with a gas-permeable, proton-conductive film; more specifically, "Nafion" (trademark, product of Dupont), which is a type of fluororesin. "Nafion" is a proton-conductive material capable of operating at low temperature and is used at portions of polymer electrolyte fuel cells.

[0004] The present inventors found that when Nafion is used as a proton-conductive layer as in the gas sensor disclosed in Japanese Patent Publication No. 7-31153, the sensor output depends on the H_2O concentration of an atmosphere of a gas under measurement (hereinafter referred to as a measurement gas atmosphere), so that accurate measurement becomes difficult. Further, the present inventors found that the above phenomena occurs because protons pass through Nafion together with H_2O molecules, and therefore the proton conductivity varies with the H_2O concentration of the measurement gas atmosphere. That is, when the proton-conductive layer is formed of Nafion, the sensor output depends on the H_2O concentration of the measurement gas atmosphere, so that the sensor output decreases greatly, especially when the H_2O concentration is low.

[0005] The present inventors further found that although porous Pt electrodes (catalysts) are generally known to exhibit high activity at low temperature (porous Pt electrodes are used in, for example, fuel cells), when such a Pt electrode is exposed to an atmosphere having a high CO concentration, CO is adsorbed on the Pt electrode, or the Pt electrode is CO-poisoned, so that the sensor output decreases greatly.

[0006] Since many fuel cells use pressurized fuel gas in order to improve power generation efficiency, sensors used in the fuel gas are required to have a small pressure dependency. However, in the sensor described in the above-mentioned Japanese Patent Publication No. 7-31153, a gas under measurement is diffused to the working electrode via the gas-permeable, proton-conductive film, so that the sensor exhibits a great pressure dependency, depending on the structure of the proton-conductive film itself, and therefore high measurement accuracy cannot be obtained.

[0007] An object of the present invention is to provide a hydrogen gas sensor capable of accurately measuring a hydrogen gas concentration in the presence of a variety of interfering gasses.

[0008] In a hydrogen gas sensor according to the present invention, a rate of conduction of protons from a first electrode to a second electrode is rendered greater than a rate at which protons are derived from hydrogen gas introduced onto the first electrode via a diffusion-rate limiting portion.

[0009] That is, since the rate of conduction of protons from the first electrode to the second electrode is sufficient greater than the rate at which protons are derived from hydrogen gas which is introduced from the measurement gas atmosphere onto the first electrode via the diffusion-rate limiting portion, the sensor can accurately measure hydrogen gas concentration without causing a great decrease in sensor output even when the measurement gas atmosphere has a low H_2O concentration or a high CO concentration.

[0010] The present invention is applicable to both a hydrogen gas sensor having no reference electrode and a hydrogen gas sensor having a reference electrode. In the latter gas sensor, the voltage applied between the first and second electrodes can be controlled variably such that a constant voltage is produced between the first electrode and the reference electrode, or such that the hydrogen gas concentration on the first electrode becomes constant. Therefore, for any given hydrogen gas concentration an optimal voltage can be applied between the first and second electrodes, so that more accurate measurement of hydrogen gas concentration can be performed within a wide range of concentration.

[0011] The hydrogen gas sensor according to the present invention is advantageously used for measurement of an atmosphere in which hydrogen gas, H_2O, and other components coexist, especially for measurement of hydrogen gas concentration of a fuel gas for polymer electrolyte fuel cells.

[0012] A preferred mode of the present invention will now be described.

[0013] In the preferred mode of the present invention, the diffusion-rate limiting portion preferably has a relatively high gas-diffusion resistance, so as to render the proton-conducting performance excessive. In this case, the rate of conduction of protons through the proton-conductive layer becomes greater than the rate at which protons are derived

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from hydrogen gas introduced onto the first electrode. The gas-diffusion resistance of the diffusion-rate limiting portion is increased through. for example, an increase in the length (thickness) of the diffusion-rate limiting portion with respect to the gas diffusion direction or a decrease in the area of a cross section taken perpendicular to the gas diffusion direction (hereinafter referred to as a "flow sectional area"). Alternatively. when the diffusion-rate limiting portion is formed of a porous material, the gas-diffusion resistance of the diffusion-rate limiting portion is increased through a decrease in the porosity (pore diameter, apparent porosity, etc.) of the porous material.

[0014] The gas-diffusion resistance of the diffusion-rate limiting portion is preferably set as follows in order to render the rate of conduction of protons from the first electrode to the second electrode greater than the rate at which protons are derived from hydrogen gas introduced onto the first electrode via the diffusion-rate limiting portion.

(1) Proton conduction condition A: A proton-conducting rate under severe conditions is measured. That is, there is measured a current (a) flowing between the first and second electrodes upon application of a sufficiently high voltage between the first and second electrodes in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered sufficiently small in order to introduce a sufficiently large amount of hydrogen gas onto the first electrode, but under the severest conditions for proton conduction; e.g., conditions such that a measurement gas atmosphere has a very low H_2O concentration (specifically, 10% or less at 80°C) or a very high CO concentration (specifically, 1000 ppm or greater). Although the above-described current (a) is not required to be a saturation current, the applied voltage (specifically, 50 mV or higher) is preferably equal to or higher than the voltage applied in the case of condition B described below.

(2) Proton conduction condition B: Next, a proton-conducting rate under favorable conditions is measured. That is, there is measured a saturation current (b) flowing between the first and second electrodes upon application of a sufficiently high voltage between the first and second electrodes in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered larger in order to sufficiently reduce the amount of hydrogen gas introduced onto the first electrode, but under favorable conditions for proton conduction, e.g., conditions such that a measurement gas atmosphere has a sufficiently high H20 concentration (specifically, 15% or greater, more preferably, 20% or greater, at 80°C) or a sufficiently low CO concentration (specifically, 800 ppm or less).

(3) Setting of gas-diffusion resistance: When the gas-diffusion resistance of the diffusion-rate limiting portion is set to a sufficiently high value under condition B, current (a) > saturation current (b). Thus. the hydrogen gas-sensor is configured such that proton-conducting rate [current value] under the severest conditions for proton conduction > proton-conducting rate under favorable conditions for proton conduction. In this hydrogen gas sensor, the proton-conducting rate is always greater than the proton-generation rate corresponding to the rate at which hydrogen gas is introduced onto the first electrode (or the largest proton-generation rate corresponding to the largest rate at which hydrogen gas is introduced onto the first electrode).

[0015] In the preferred mode of the present invention, a current (c) flowing between the first and second electrodes is measured under sever conditions for proton conduction; current (d) flowing between the first and second electrodes is measured under favorable conditions for proton conduction; and the gas-diffusion resistance of the diffusion-rate limiting portion is set such that the ratio of current (d) to current (c) (= current (d)/current(c)) or its reciprocal (= current (c)/current(d)) approaches 1. Thus, the H_2O-concentration dependency and CO-concentration dependency of the current flowing through the first and second electrodes decrease. Preferably, the gas-diffusion resistance of the diffusion-rate limiting portion and/or the area of the first or second electrode is properly set, or a predetermined solution is applied to the interface of the first or second electrode which is in contact with the proton-conductive layer, such that the ratio [saturation current flowing between the first and second electrodes at H_2O = 30%]/[saturation current flowing between the first and second electrodes at H_2O = 10%] falls within the range of 1 to 1.15, more preferably, 1 to 1.1, most preferably, 1 to 1.05. Further, preferably, the gas-diffusion resistance of the diffusion-rate limiting portion and/or the area of the first or second electrode is properly set, or a predetermined solution is applied to the interface of the first or second electrode which is in contact with the proton-conductive layer, such that the ratio [saturation current flowing between the first and second electrodes at CO = 1000 ppm]/[saturation current flowing between the first and second electrodes at CO = 0 ppm] falls within the range of 0.9 to 1 (the reciprocal of the rate falls within the range of 1 to 1.1), more preferably, 0.95 to 1 (the reciprocal of the rate falls within the range of 1 to 1.05). Thus, a layer containing a polymer electrolyte is formed at the interface.

[0016] In the preferred mode of the present invention, the first and second electrodes are formed in an opposed manner to sandwich the proton-conductive layer. This structure reduces the resistance between the first and second electrodes to thereby improve the proton-conducting performance of the proton-conductive layer. However, when the gas-diffusion resistance of the diffusion-rate limiting portion is excessively high, the sensitivity of the hydrogen gas sensor lowers. Therefore, the area of at least one of the first and second electrodes is preferably increased, when the sensor must have a relatively high sensitivity. Further, the first and second electrodes may be formed on the same plane of the proton-conductive layer, if a sufficient degree of sensitivity can be secured.

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[0017] In the preferred mode of the present invention, a solution containing a polymer electrolyte identical with that of the proton-conductive layer is applied to the side of each electrode in contact with the proton-conductive layer (the interface between each electrode and the proton-conductive layer). This increases the contact area between the proton-conductive layer and catalytic components carried on the electrode. so that the proton-conducting performance is increased further. Further, the proton-conducting performance may be enhanced through a decrease in thickness of the proton-conductive layer.

[0018] In the preferred mode of the present invention, the proton-conductive layer is a polymer electrolytic proton-conductive layer which operates sufficiently at relatively low temperature, for example, temperatures not greater than 150°C, preferably, at temperatures not greater than 130°C, more preferably, at around 80°C; e.g., a proton-conductive layer formed of a resin-based solid polymer electrolyte.

[0019] In the preferred mode of the present invention, a proton-conductive layer is formed of one or more types of fluororesins, more preferably of "Nafion" (trademark, product of Dupont).

[0020] In the preferred mode of the present invention, each electrode is a porous electrode formed of carbon or any other suitable material and carries a catalyst such as Pt on the side in contact with the proton-conductive layer.

[0021] In the preferred mode of the present invention, the proton-conductive layer, the respective electrodes, and the diffusion-rate limiting portion are supported on a support to thereby constitute an integrated hydrogen gas sensor. The support is formed of an inorganic insulating material such as an alumina ceramic or an organic insulating material such as resin. Further, the diffusion-rate limiting portion is preferably formed of a porous alumina ceramic or a like material having gas permeability, or alternatively may be formed of small holes each having a small flow sectional area, such as one or more through-holes each having a very small opening diameter, which are formed at a portion of the support formed of a dense body. Such fine through-holes can be formed by use of, for example, laser machining or ultrasonic machining. In the case of laser machining, the opening diameter may be adjusted by controlling the irradiation diameter, output power, time, etc., of a laser beam. The average pore diameter of the porous material and the opening diameter of the through-holes are preferably not less than 1 μm. In this case, since gas diffusion proceeds outside the region of Knudsen diffusion, the pressure dependency of the sensor can be lowered.

[0022] The hydrogen gas sensor of the present invention can be fabricated through a process such that the proton-conductive layer and the respective electrodes are physically sandwiched between two supports such that the respective electrodes come into contact with the proton-conductive layer. Alternatively, the respective electrodes may be bonded to the proton-conductive layer by means of hot pressing.

[0023] In the preferred mode of the present invention, a hydrogen gas sensor provided with no reference electrode has a support for supporting the proton-conductive layer, the first electrode, the second electrode, and the diffusion-rate limiting portion, and a hydrogen gas sensor provided with a reference electrode has a support for supporting the proton-conductive layer, the first electrode, the second electrode, the reference electrode, and the diffusion-rate limiting portion.

[0024] Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Fig. 1 is a sectional view of a main portion of a hydrogen gas sensor according to the present invention;
Fig. 2 is a graph in relation to results of measurement 1, showing an applied voltage-current characteristic for each of various hydrogen gas concentrations;
Fig. 3 is a graph in relation to results of measurement 2-1, showing the relationship between flow sectional area of the diffusion-rate limiting portion and current (sensitivity) at H_2 = 40%;
Fig. 4 is a graph in relation to results of measurement 2-2, showing the dependency of current (sensitivity) on flow sectional area (gas-diffusion resistance) of the diffusion-rate limiting portion and H_2O concentration;
Fig. 5 is a graph in relation to results of measurement 2-3, showing the dependency of current (sensitivity) on flow sectional area (gas-diffusion resistance) of the diffusion-rate limiting portion and CO concentration;
Fig. 6 is a graph in relation to results of measurement 3, showing the dependency of current (sensitivity) on electrode area and H_2O concentration;
Fig. 7 is a graph in relation to measurement 4, showing the relationship between H_2O concentration and resistance between the first and second electrodes for the case where a solution was applied and for the case where the solution was not applied;
Fig. 8 is a sectional view of a main portion of another hydrogen gas sensor according to the present invention;
Fig. 9 is a graph in relation to results of measurement 5, showing the relationship between hydrogen gas concentration and current (current flowing between the first and second electrodes) at each of different H_2O concentrations;
Fig. 10 is a graph in relation to results of measurement 5, showing the relationship between hydrogen gas concentration and applied voltage at each of different H20 concentrations; and
FIG. 11 is a graph in relation to measurement 6, showing the relationship between gas pressure and current (current

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flowing between the first and second electrodes) measured for each of different pore diameters of the diffusion-rate limiting portion.

[0025] Reference numerals are used in the drawings to identify items as follows:

1a, 1b:	upper and lower supports
2:	proton-conductive layer
3:	first electrode
4:	second electrode
5:	reference electrode
6:	diffusion-rate limiting portion
7:	power source
8:	ammeter
9:	power source
10:	voltmeter
11:	aperture

[0026] First, the structure of a hydrogen gas sensor according to the present invention will be described. FIG. 1 is a sectional view of a main portion of the hydrogen gas sensor. As shown in FIG. 1, in the hydrogen gas sensor, a first electrode 3 and a second electrode 4 are disposed on opposite surfaces, respectively, of a proton-conductive layer 2 such that the first electrode 3 and the second electrode 4 sandwich the proton-conductive layer 2. Further, an upper support 1a and a lower support 1b sandwich the first electrode 3 and the second electrode 4. A diffusion-rate limiting portion 6 is formed in the upper support 1a to be located above the first electrode 3. The diffusion-rate limiting portion 6 is provided to be located between the first electrode 3 and a measurement gas atmosphere, and the second electrode 4 is in contact with the measurement gas atmosphere via an aperture 11 formed in the lower support 1b.

[0027] A series circuit comprising a power source 7 and an ammeter 8 is connected between the first and second electrodes 3 and 4 via lead portions, so that a voltage is applied between the first and second electrodes 3 and 4, and current flowing between the first and second electrodes 3 and 4 can be measured.

[0028] Next, the measurement principle of the hydrogen gas sensor will be described with reference to FIG. 1.

(1) Hydrogen gas having reached the first electrode 3 via the gas-diffusion-rate limiting portion 6 is dissociated into protons by virtue of the catalytic action of a catalytic component such as Pt carried on the first electrode 3 and the voltage applied between the first electrode 3 and the second electrode 4.

(2) The generated protons are conducted to the second electrode 4 via the proton-conductive layer 2 and are converted to hydrogen gas on the second electrode 4, which hydrogen gas diffuses into the measurement gas atmosphere via the aperture 11. When the applied voltage mentioned is sufficiently high so that saturation current flows between the first electrode 3 and the second electrode 4, the current flowing between the first electrode 3 and the second electrode 4 varies in proportion to the hydrogen gas concentration. Therefore, the hydrogen gas concentration can be measured through detection of the saturation current by use of the ammeter 8.

[0029] Measurement of hydrogen gas concentration was performed by use of the above-described hydrogen gas sensor (see FIG. 1). In the hydrogen gas sensor, the proton-conductive layer was formed of the above-described Nafion; the first and second electrodes were porous carbon electrodes carrying a catalyst such as Pt on the side in contact with the proton-conductive layer; the support was formed of dense alumina ceramic; and the diffusion-rate limiting portion was formed of porous alumina ceramic.

Measurement 1

[0030] For each of various hydrogen gas concentrations (hydrogen gas concentrations of a gas under measurement), current flowing between the first and second electrodes 3 and 4 was measured, while the voltage applied between the first and second electrodes 3 and 4 was varied. Measurement conditions were as follows.

Measurement Conditions
Gas composition: H_2 (0-40%), CO_2 (15%), H_2O (25%), N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min; and
Applied voltage: 0-800 mV.

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[0031] Next, results of the measurement will be described. FIG. 2 is a graph showing an applied voltage/current characteristic for each of various hydrogen gas concentrations. As is understood from FIG. 2, saturation current flows when the applied voltage exceeds about 400 mV, and the magnitude of the saturation current varies in proportion to the hydrogen gas concentration. Therefore, the hydrogen gas concentration can be measured by use of the hydrogen gas sensor.

Embodiment 1, Measurement 2

[0032] Next, with reference to the following measurement results, there will be described an example method of rendering the rate of conduction of protons from the first electrode to the second electrode greater than the rate at which hydrogen gas is introduced onto the first electrode via the diffusion-rate limiting portion, as well as the effect thereof.

Measurement 2-1

[0033] The structure of hydrogen gas sensors used in the present measurement will be described. Hydrogen gas sensors having the above-described structure (see FIG. 1) but differing from one another in terms of gas-diffusion resistance of the diffusion-rate limiting portion were fabricated. Specifically, the cross sectional area of the diffusion-rate limiting portion as measured perpendicular to the gas diffusion direction was changed among the hydrogen gas sensors. The same voltage was applied between the first and second electrodes 3 and 4 of each hydrogen gas sensor, and current flowing between the first and second electrodes 3 and 4 was measured. Measurement conditions were as follows.

Measurement Conditions
Gas composition: H_2 (40%), CO_2 (15%), H_2O (20%), N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min; and
Applied voltage: 800 mV.

[0034] Next, results of the measurement will be described. FIG. 3 is a graph showing the relationship between the flow sectional area of the diffusion-rate limiting portion and current (sensitivity) at H_2=40%. As is understood from FIG. 3, the current decreases with the flow sectional area of the diffusion-rate limiting portion, and therefore, the amount of hydrogen gas introduced onto the first electrode can be reduced through an increase in the gas-diffusion resistance of the diffusion-rate limiting portion.

Measurement 2-2

[0035] At each of various H_2O concentrations, a measurement similar to measurement 2-1 was performed by use of the gas sensors used in measurement 2-1. Measurement conditions were as follows.

Measurement Conditions
Gas composition: H_2 (40%), CO_2 (15%), H_2O (10, 20, 30%).
N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min; and
Applied voltage: 800 mV.

[0036] FIG. 4 is a graph provided for describing results of measurement 2-2 and showing the dependency of current (sensitivity) on the flow sectional area (gas-diffusion resistance) of the diffusion-rate limiting portion and H_2O concentration. Since the absolute value of current (sensitivity) varies with the flow sectional area, each of currents (sensitivities) at H_2O =20% and 30% is represented as a ratio to current (sensitivity) at H_2O =10%. The absolute values of the respective currents are shown in Table 1.

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Table 1

	Current (Absolute value) [mA]		
	Sectional area of diffusion-rate limiting portion		
H_2O concentration	4.3 mm^2	2.7 mm^2	1.4 mm^2
10% (c)	7.316 (a)	2.097	0.665
20%	8.296	2.173	0.688
30% (d)	8.671	2.247	0.693 (b)

(a) Current under Proton conduction condition A; i.e., low gas-diffusion resistance of the diffusion-rate limiting portion, and severe conditions for proton conduction;

(b) Current under Proton conduction condition B; i.e., high gas-diffusion resistance of the diffusion-rate limiting portion, and favorable conditions for proton conduction;

(c) Severe conditions for proton conduction; and

(d) Favorable conditions for proton conduction.

[0037] As is understood from FIG. 4, the H_2O-concentration dependency decreases with the flow sectional area of the diffusion-rate limiting portion. Therefore, when the gas-diffusion resistance of the diffusion-rate limiting portion is increased to thereby render the proton-conductive performance excessive relative to the proton generation rate, the H_2O-concentration dependency of the sensitivity or detection output of the sensor can be reduced. Further, Table 1 demonstrates that since current (a) > current (b), the rate of conduction of protons from the first electrode to the second electrode is greater than the rate at which protons are derived from hydrogen gas which is introduced onto the first electrode via the diffusion-rate limiting portion. Further, as shown in FIG. 4, for H_2O = 30%, the current ratio (current (d)/current (c)) was 1.185 when the sectional area of the diffusion-rate limiting portion was 4.3 mm^2, 1.071 when the sectional area was 2.7 mm^2, and 1.041 when the sectional area was 1.4 mm^2.

Measurement 2-3

[0038] The CO-concentration dependency of current (sensitivity) was investigated by use of the gas sensors used in measurement 2-2. Specifically, at each of various CO concentrations, a measurement similar to measurement 2-2 was performed. Measurement conditions were as follows.

Measurement Conditions
Gas composition: H_2 (40%), CO_2 (15%), H_2O (25%), CO (0, 1000 ppm), N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min; and
Applied voltage: 800 mV.

[0039] FIG. 5 is a graph provided for describing results of measurement 2-3 and showing the dependency of current (sensitivity) on the flow sectional area (gas-diffusion resistance) of the diffusion-rate limiting portion and CO concentration. Since the absolute value of current (sensitivity) varies with the flow sectional area, current (sensitivity) at CO

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= 1000 ppm is represented as a ratio to current (sensitivity) at CO = 0 ppm.

[0040] As is understood from FIG. 5, the CO-concentration dependency decreases with the flow sectional area of the diffusion-rate limiting portion. Therefore, when the gas-diffusion resistance of the diffusion-rate limiting portion is increased to thereby render the proton-conductive performance excessive relative to the proton generation rate, the influence of CO-poisoning of Pt serving an electrode catalyst can be reduced. Further, as shown in FIG. 5, the current ratio (current (c: CO = 1000 ppm)/current (d: CO = 0 ppm)) was 0.8785 (the reciprocal was 1.138) when the sectional area of the diffusion-rate limiting portion was 4.3 mm^2, 0.9813 (the reciprocal was 1.019) when the sectional area was 2.7 mm^2, and 0.99996 (the reciprocal was 1.00003) when the sectional area was 1.4 mm^2.

[0041] As described above, since the gas-diffusion resistance of the diffusion-rate limiting portion is increased to thereby render the proton-conductive performance excessive relative to the proton generation rate, the influences of, for example, H_2O and CO present in a measurement gas atmosphere can be reduced, whereby more accurate measurement of hydrogen gas concentration is enabled. The above-described method of increasing the gas-diffusion resistance is a mere example, and the gas-diffusion resistance may be increased through an increase in the length of the diffusion-rate limiting portion with respect to the gas diffusion direction or through a decrease in the pore diameter or porosity (open-pore ratio) of the porous material that constitutes the diffusion-rate limiting portion.

Embodiment 2, Measurement 3

[0042] Next, there will be described an example method in which the proton-conducting performance itself is improved in order to render the rate of conduction of protons from the first electrode to the second electrode greater than the rate at which hydrogen gas is introduced onto the first electrode.

[0043] The structure of hydrogen gas sensors used in the present measurement will next be described. Hydrogen gas sensors having the above-described structure (see FIG. 1) but differing from one another in terms of the areas of the first and second electrodes were fabricated. A measurement similar to measurement 2-2 was performed by use of the thus-fabricated hydrogen gas sensors.

[0044] FIG. 6 is a graph provided for describing results of measurement 3 and showing the dependency of current (sensitivity) on electrode area and H_2O concentration. For each electrode area, each of currents (sensitivities) at H_2O =20% and 30% is represented as a ratio to current (sensitivity) at H_2O =10%.

[0045] As is understood from FIG. 6, when the electrode area is made about double, the proton-conducting performance is improved, so that the H_2O-concentration dependency of the gas sensor sensitivity can be reduced greatly.

Embodiment 3, Measurement 4

[0046] Next, there will be described an example method in which a solution containing a polymer electrolyte that constitutes the proton-conductive layer is applied to the sides of the first or second electrode which are in contact with the proton-conductive layer (at interfaces), in order to improve the proton-conducting performance itself, whereby the rate of conduction of protons from the first electrode to the second electrode is rendered greater than the rate at which hydrogen gas is introduced onto the first electrode.

[0047] The structure of hydrogen gas sensors used in the present measurement will next be described. There were fabricated hydrogen gas sensors which had the above-described structure (see FIG. 1) and in which a mixed solution of Nafion (5 wt.%), water, and aliphatic lower alcohol was applied to the sides of the first or second electrode in contact with the proton-conductive layer, as well as hydrogen gas sensors which had the above-described structure and in which the mixed solution was not applied. The resistance between the first and second electrodes was measured at each of various H_2O concentrations by use of the thus-fabricated hydrogen gas sensors. Measurement conditions were as follows. The area of the first electrode was the same as that of the second electrode.

Measurement Conditions
Gas composition: H_2 (40%), CO_2 (15%), H_2O (10-30%), N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min: and
Resistance between first and second electrode:
applied voltage (50 mV)/current.

[0048] FIG. 7 is a graph provided for describing results of measurement 4 and showing the relationship between H_2O concentration and resistance between the first and second electrodes for the case where the solution was applied and for the case where the solution was not applied. The resistance between the first and second electrodes was determined from current that flowed upon application of 50 mV.

[0049] As is understood from FIG. 7, when a solution containing a predetermined polymer electrolyte is applied onto

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the electrode surface, the contact area between the proton-conductive layer and the electrodes increases, so that within a wide range of H_2O concentration, the resistance between the first and second electrodes can be reduced to thereby improve the proton-conducting performance.

[0050] As described above, since a solution containing a predetermined polymer electrolyte is applied onto the electrode surface to thereby render the proton-conductive performance excessive, the influences of, for example, H_2O and CO present in a measurement gas atmosphere can be reduced, whereby more accurate measurement of hydrogen gas concentration is enabled.

[0051] Further, the results of measurements 2-4 demonstrate that when the flow sectional area of the diffusion-rate limiting portion and the electrode surface of the first and second electrodes are optimized and a solution containing a polymer electrolyte is applied onto the electrode surface, the proton-conductive performance is improved in both relative and absolute terms, so that hydrogen gas concentration can be measured more accurately.

[0052] Next, the structure of another hydrogen gas sensor according to the present invention will be described. This second hydrogen gas sensor differs from the hydrogen gas sensor shown in FIG. 1 in that a reference electrode is provided. FIG. 8 is a sectional view of a main portion of the second hydrogen gas sensor. In FIG. 8, elements having the same functions as those shown in FIG. 1 are denoted by the same reference numerals.

[0053] As shown in FIG. 8, in the second hydrogen gas sensor, a first electrode 3 and a second electrode 4 are disposed on opposite surfaces, respectively, of a proton-conductive layer 2 such that the first electrode 3 and the second electrode 4 sandwich the proton-conductive layer 2. A reference electrode 5 is formed on the surface of the proton-conductive layer 2 on which the second electrode 4 is formed. Further, an upper support 1a and a lower support 1b sandwich the first electrode 3, the second electrode 4, and the reference electrode 5. A diffusion-rate limiting portion 6 is formed in the upper support 1a to be located above the first electrode 3. The diffusion-rate limiting portion 6 is provided to be located between the first electrode and a measurement gas atmosphere, and the second electrode 4 is in contact with the measurement gas atmosphere via an aperture 11 formed in the lower support lb. The reference electrode 5 is formed such that the reference electrode 5 is in contact with the proton-conductive layer 2 and is not exposed directly to a measurement gas atmosphere. The reference electrode 5 provides a reference potential.

[0054] A series circuit comprising a power source 9 and an ammeter 8 is connected between the first and second electrodes 3 and 4 via lead portions, so that a voltage is applied between the first and second electrodes 3 and 4, and current flowing between the first and second electrodes 3 and 4 can be measured. A voltmeter 10 is connected between the first electrode 3 and the reference electrode 5 via lead portions. Further, a control circuit is formed between the voltmeter 10 and the power source 9 in order to variably control the voltage applied between the first and second electrodes 3 and 4 in accordance with the potential difference between the first electrode 3 and the reference electrode 5.

[0055] Next, the measurement principle of the hydrogen gas sensor having a reference electrode will be described with reference to FIG. 8.

(1) When hydrogen gas reaches the first electrode 3 via the gas-diffusion-rate limiting portion 6, an electromotive force corresponding to the hydrogen gas concentration is generated between the first electrode 3 and the reference electrode 5 across the proton-conductive layer 2.

(2) A control voltage is applied between the first electrode 3 and the second electrode 4 such that the hydrogen gas concentration on the first electrode 3 becomes constant; i.e., the potential difference between the first electrode 3 and the reference electrode 5 becomes constant.

(3) The hydrogen gas having reached the first electrode 3 via the gas-diffusion-rate limiting portion 6 is dissociated into protons by virtue of the catalytic action of the catalytic component, such as Pt, carried on the first electrode 3 and the voltage applied between the first electrode 3 and the second electrode.

(4) The generated protons are conducted to the second electrode 4 via the proton-conductive layer 2 and are converted to hydrogen gas on the second electrode 4, which hydrogen gas diffuses into the measurement gas atmosphere via the aperture 11. When the above-described voltage applied in a controlled manner is sufficiently high so that saturation current flows between the first electrode 3 and the second electrode 4, the current flowing between the first electrode 3 and the second electrode 4 varies in proportion to the hydrogen gas concentration. Therefore, the hydrogen gas concentration can be measured through detection of the saturation current by use of the ammeter 8.

[0056] Since the voltage applied between the first and second electrodes 3 and 4 is controlled such that the hydrogen gas concentration on the first electrode 3 is maintained constant, high voltage can be applied when the hydrogen gas concentration of the gas under measurement is high, and low voltage can be applied when the hydrogen gas concentration of the gas under measurement is low. In other words, optimal voltage can be applied between the first and second electrodes 3 and 4 in accordance with hydrogen gas concentration. Further, in the gas sensor having the reference electrode (see FIG. 8), when the resistance between the first and second electrodes 3 and 4 increases for

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some reason, the applied voltage automatically changes properly, or can be changed properly. Therefore, hydrogen gas concentration can be measured accurately, while the influence of H_2O and the like is suppressed further.

Embodiment 4, Measurement 5

[0057] Next, results of measurement performed by use of the hydrogen gas sensor having a reference electrode (see FIG. 8) will be described. In the hydrogen gas sensor, the proton-conductive layer was formed of the above-described Nafion; the first and second electrodes and the reference electrode were porous carbon electrodes carrying a catalyst such as Pt on the side in contact with the proton-conductive layer; the support was formed of dense alumina ceramic: and the diffusion-rate limiting portion was formed of porous alumina ceramic.

[0058] Further, in order to stabilize the hydrogen gas concentration on the reference electrode, the reference electrode was caused to serve as a self-generation reference electrode. Specifically, a constant small current was caused to flow from the first electrode to the reference electrode to thereby supply protons to the reference electrode, whereby a portion of hydrogen gas generated on the reference electrode was leaked to the outside via a predetermined leakage resistance portion (small hole).

[0059] Moreover, as in the above-described embodiments 1 to 3, the flow sectional area of the diffusion-rate limiting portion and the electrode surface of the first and second electrodes were optimized, and a solution containing a polymer electrolyte was applied onto the surfaces of the first and second electrodes in contact with the proton-conductive layer, so that that the proton-conductive performance was improved in both relative and absolute terms. Specifically, the flow sectional area of the diffusion-rate limiting portion was set to 1.4 mm^2, the electrode area of the first electrode was set to 14 mm^2, and the electrode area of the second electrode was set to 10 mm^2.

[0060] For each of various H_2O concentrations (H_2O concentrations of a gas under measurement), current flowing between the first and second electrodes was measured, while hydrogen gas concentration was varied. Measurement conditions were as follows.

Measurement Conditions
Gas composition: H_2 (0-40%), CO_2 (15%), H_2O (10-30%),
N_2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min;
Potential difference between first electrode and reference electrode (control target): 150 mV; and
Constant current for self-generation reference electrode: 10 μA

[0061] FIG. 9 is a graph provided for describing results of measurement 5 and showing the relationship between hydrogen gas concentration and current (current flowing between the first and second electrodes) at each of different H_2O concentrations. FIG. 10 shows the voltage (control voltage applied between the first and second electrodes) at that time.

[0062] As is understood from FIG. 9, current curves for different H_2O concentrations become substantially identical over a wide range of hydrogen gas concentration. This indicates that when the reference electrode is disposed and the rate of proton conduction between the first and second electrodes is render sufficiently high, accurate measurement of hydrogen gas concentration becomes possible, while influences of H_2O, etc. are reduced.

[0063] As is understood from FIG. 10, the voltage applied between the first and second electrodes varies with hydrogen gas concentration, and the applied voltage increases as H_2O concentration decreases. Therefore, provision of the reference electrode enables application of an optimal voltage between the first and second electrodes even when the conditions of a measurement gas atmosphere; e.g., gas composition, varies.

Embodiment 5, Measurement 6

[0064] Next will be described results of measurement in which the gas pressure dependency of the hydrogen gas sensor having a reference electrode (see FIG. 8) was measured by use of hydrogen gas sensors whose diffusion-rate limiting portions had different pore diameters (opening diameters). Since Embodiment 5 is the same as Embodiment 4 excepting points which will be described in detail below, a repeated description will be omitted.

[0065] The diffusion-rate limiting portion of each sensor was constituted of a porous alumina ceramic having an average pore diameter of 0.31 μm or 1 μm or a dense alumina ceramic having through-holes each having an opening diameter of 30 μm, 50 μm, or 70 μm. The pore diameter and the opening diameter were measured through observation by use of a scanning electron microscope (SEM). A measurement gas was supplied under a different gas pressure to each of the hydrogen gas sensors whose diffusion-rate limiting portions had different pore or opening diameters, and the current flowing between the first and second electrodes was measured. Since the absolute value of the current

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varied depending on the pore diameter (opening diameter) of the diffusion-rate limiting portion, a ratio of the current at a pressure of 2.5 atm to that at a pressure of 1 atm was measured as a current ratio. The smaller the current ratio, the smaller the evaluated gas pressure dependency. Measurement conditions were as follows.

<Measurement Conditions>

[0066]

Gas composition: H2 (40%), CO2 (15%). H2O (15%), N2 (bal.);
Gas temperature: 80°C;
Gas flow rate: 4 L/min;
Gas pressure: 1 atm, 2.5 atm
Potential difference between first electrode and reference electrode (control target): 150 mV; and
Constant current for self-generation reference electrode: 10 μA

[0067] FIG. 11 is a graph provided for describing results of measurement 6 and showing the current ratio (relative ratio of current flowing between the first and second electrodes) obtained by changing the gas pressure. As is understood from FIG. 11, the gas pressure dependency decreases greatly when the pore diameter (opening diameter) of the diffusion-rate limiting portion is 1 μm or greater.

[0068] The present invention provides a hydrogen gas sensor capable of accurately measuring a hydrogen gas concentration in the presence of a variety of interfering gasses. Further, use of the hydrogen gas sensor of the present invention enables accurate measurement of hydrogen gas concentration of a fuel gas used for polymer electrolyte fuel cells.

[0069] Having described specific preferred embodiments of the present invention, it is to be understood that the invention is not limited to those precise embodiments, and that various changes and modifications may be effected therein by one skilled in the art without departing from the scope of the invention as defined in the appended claims.

Claims

1. A hydrogen gas sensor comprising:

a proton-conductive layer formed of a polymer electrolyte;
first and second electrodes provided in contact with the proton-conductive layer; and
a diffusion-rate limiting portion disposed between the first electrode and an atmosphere of a gas under measurement,
wherein, through application of a voltage between the first and second electrodes, hydrogen gas introduced from the atmosphere onto the first electrode via the diffusion-rate limiting portion is caused to undergo dissociation, decomposition, or reaction, and the hydrogen gas concentration is determinable on the basis of a saturation current which flows as a result of conduction of produced protons from the first electrode to the second electrode via the proton-conductive layer, and
wherein a rate at which protons can be conducted from the first electrode to the second electrode is greater than a rate at which protons are derivable from hydrogen gas introduced onto the first electrode via the diffusion-rate limiting portion.

2. A hydrogen gas sensor comprising:

a proton-conductive layer formed of a polymer electrolyte;
first and second electrodes and a reference electrode provided in contact with the proton-conductive layer; and
a diffusion-rate limiting portion disposed between the first electrode and an atmosphere of a gas under measurement,
wherein, through application of a voltage between the first and second electrodes such that a constant voltage is produced between the first electrode and the reference electrode, hydrogen gas is caused to undergo dissociation, decomposition, or reaction on the first or second electrode, and the hydrogen gas concentration is determinable on the basis of a saturation current which flows as a result of conduction of produced protons via the proton-conductive layer, and
wherein a rate at which protons can be conducted from the first electrode to the second electrode is greater

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than a rate at which protons are derivable from hydrogen gas introduced onto the first electrode via the diffusion-rate limiting portion.

3. A hydrogen gas sensor according to Claim 1 or 2, wherein the proton conduction rate is not substantially affected by H_2O concentration or CO concentration in the gas under measurement.

4. A hydrogen gas sensor according to any one of the preceding Claims, wherein a solution containing a polymer electrolyte is present at an interface between the proton-conductive layer and the first electrode and/or the second electrode.

5. A hydrogen gas sensor according to any one of the preceding Claims, wherein the first and second electrodes are positioned in an opposed manner to sandwich the proton-conductive layer therebetween.

6. A hydrogen gas sensor according to any one of the preceding Claims, wherein

a current (a) flowing between the first and second electrodes is measured under sever conditions for proton conduction, upon application of a sufficiently high voltage between the first and second electrodes in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered sufficiently small;
a saturation current (b) flowing between the first and second electrodes is measured under favorable conditions for proton conduction, upon application of a sufficiently high voltage between the first and second electrodes in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered larger; and
the gas-diffusion resistance of the diffusion-rate limiting portion is set on the basis of results of both the measurements, such that the current (a) > the saturation current (b).

7. A hydrogen gas sensor according to Claim 6, wherein the gas-diffusion resistance of the diffusion-rate limiting portion is set on the basis of results of both the measurements, such that the ratio of current (a) to the saturation current (b) is in the range of from 1 to 1.15.

8. A hydrogen gas sensor according to any one of the preceding Claims, used for measurement of hydrogen gas concentration of a fuel gas for a polymer electrolyte fuel cell.

9. A hydrogen gas sensor according to any one of the preceding Claims, wherein the gas diffusion resistance of the diffusion-rate limiting portion is set such that the saturation current which flows between the first and second electrodes, upon application of a sufficiently high voltage between the first and second electrodes, in the presence of said diffusion-rate limiting portion, under favorable conditions for proton conduction, is lower than a current which can flow between the first and second electrodes, in the absence of a diffusion-rate limiting portion, or with a diffusion-rate limiting portion of low gas-diffusion resistance, but under sever conditions for proton conduction.

10. A method of selecting the gas-diffusion resistance of the diffusion-rate limiting portion of a hydrogen gas sensor according to any one of the preceding Claims, comprising the steps of:

measuring a current (a) flowing between the first and second electrodes under sever conditions for proton conduction, upon application of a sufficiently high voltage between the first and second electrodes in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered small;
measuring a saturation current (b) flowing between the first and second electrodes under favorable conditions for proton conduction, upon application of a sufficiently high voltage between the first and second electrodes, in a state in which the gas-diffusion resistance of the diffusion-rate limiting portion is rendered larger; and
selecting the gas-diffusion resistance of the diffusion-rate limiting portion such that, when the saturation current (b) is measured with the selected gas-diffusion resistance, the current (a) > the saturation current (b).

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Fig. 1

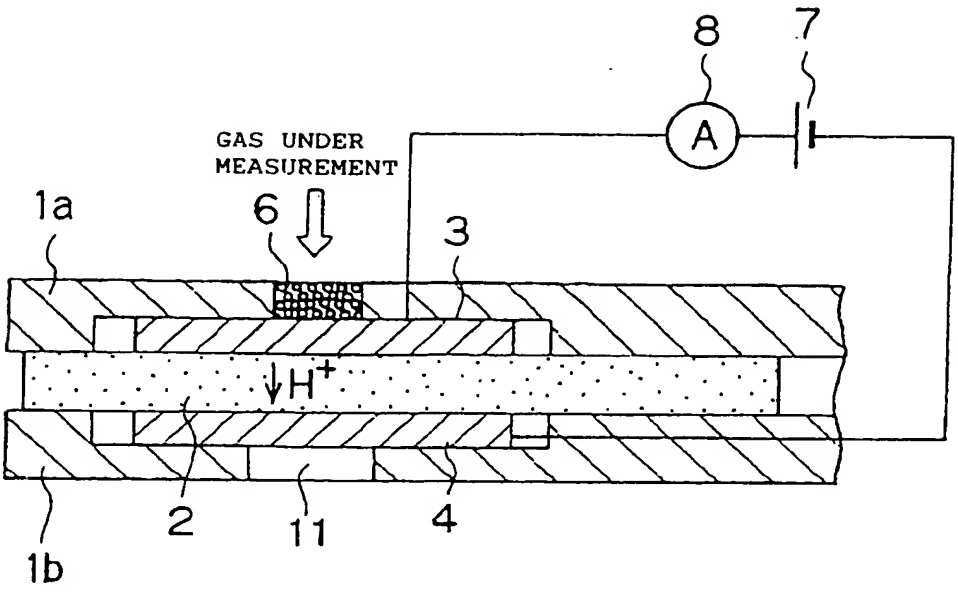

Fig. 2

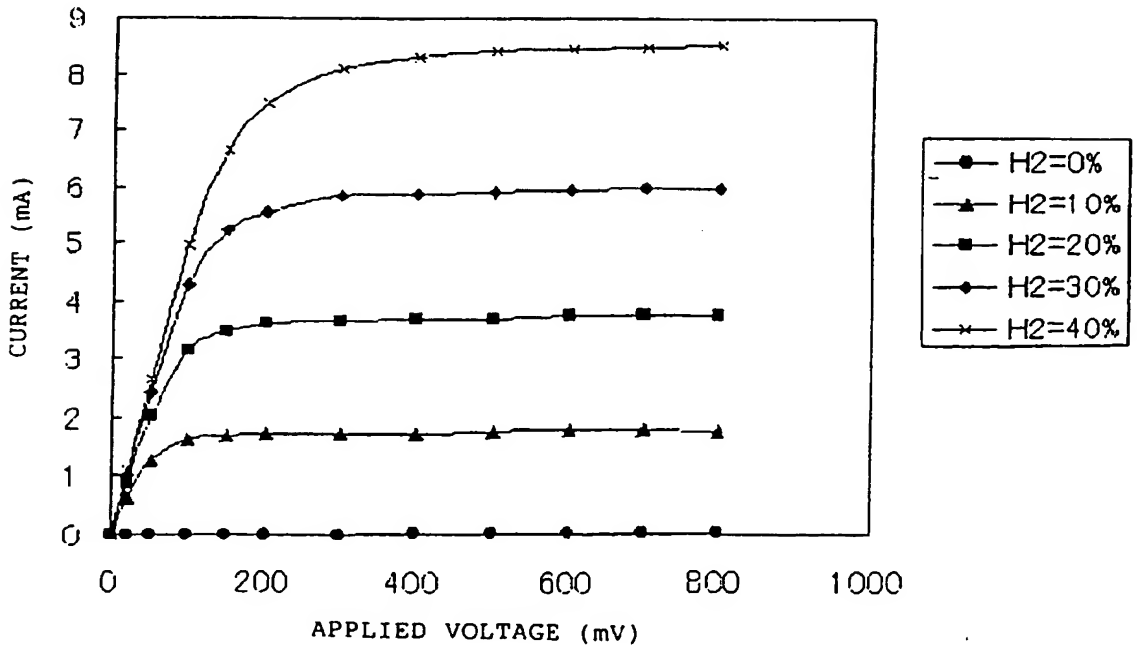

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Fig. 3

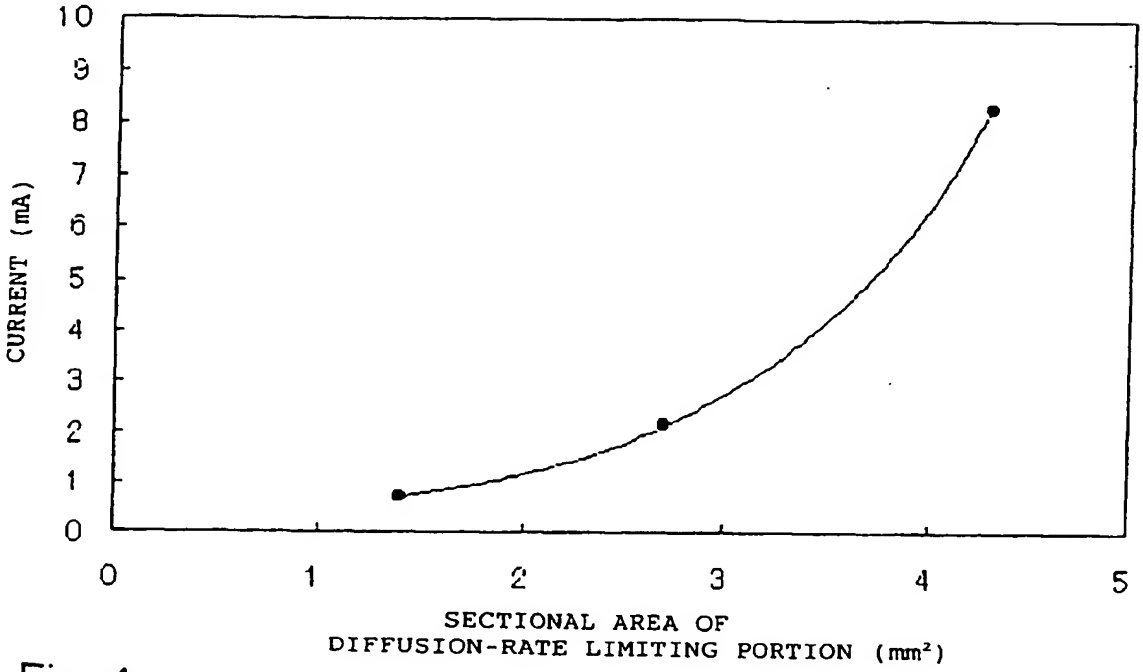

Fig. 4

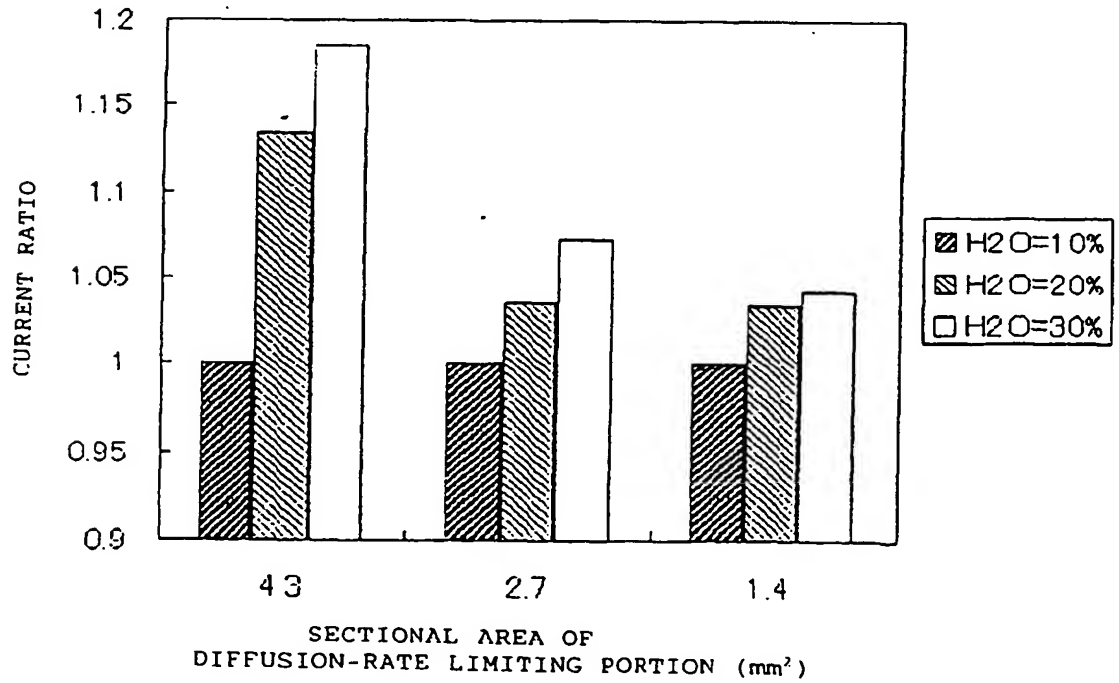

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Fig. 5

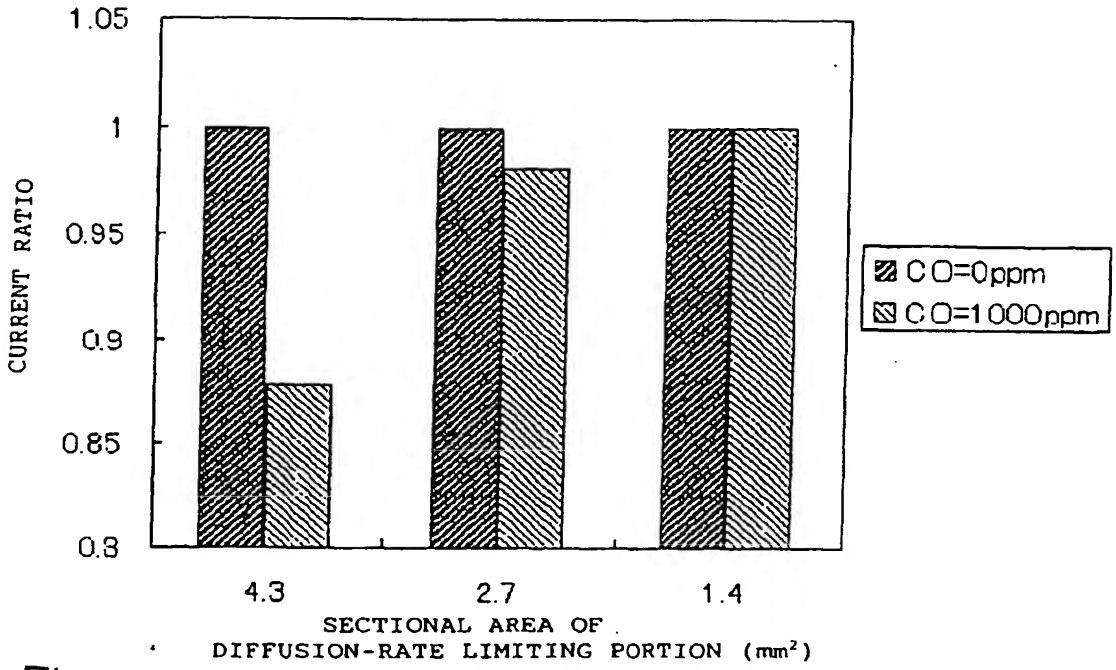

Fig. 6

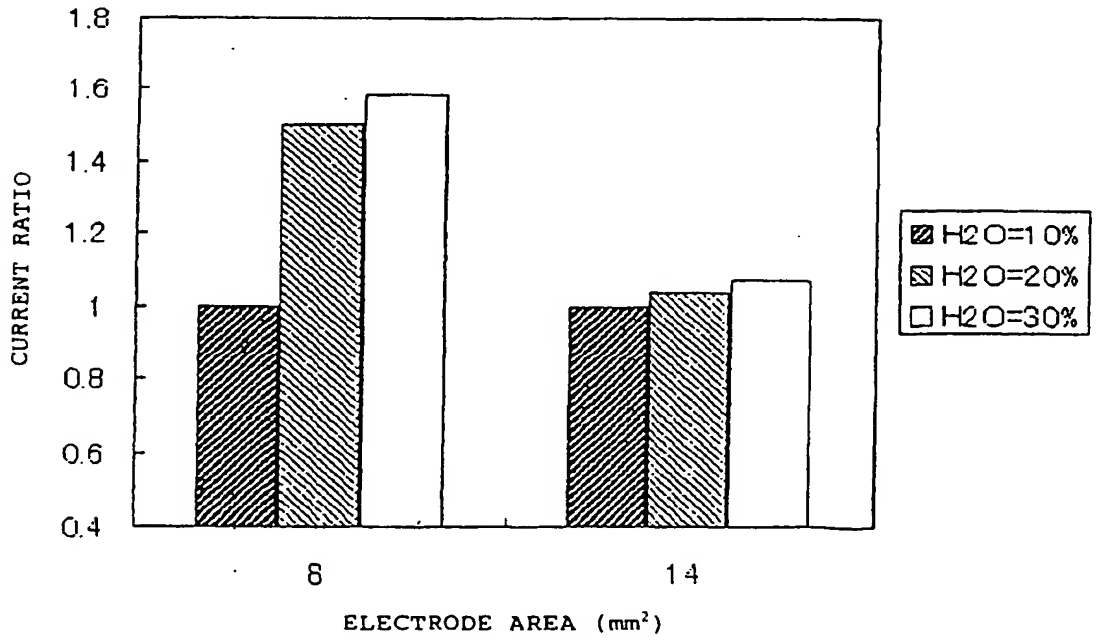

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Fig. 7

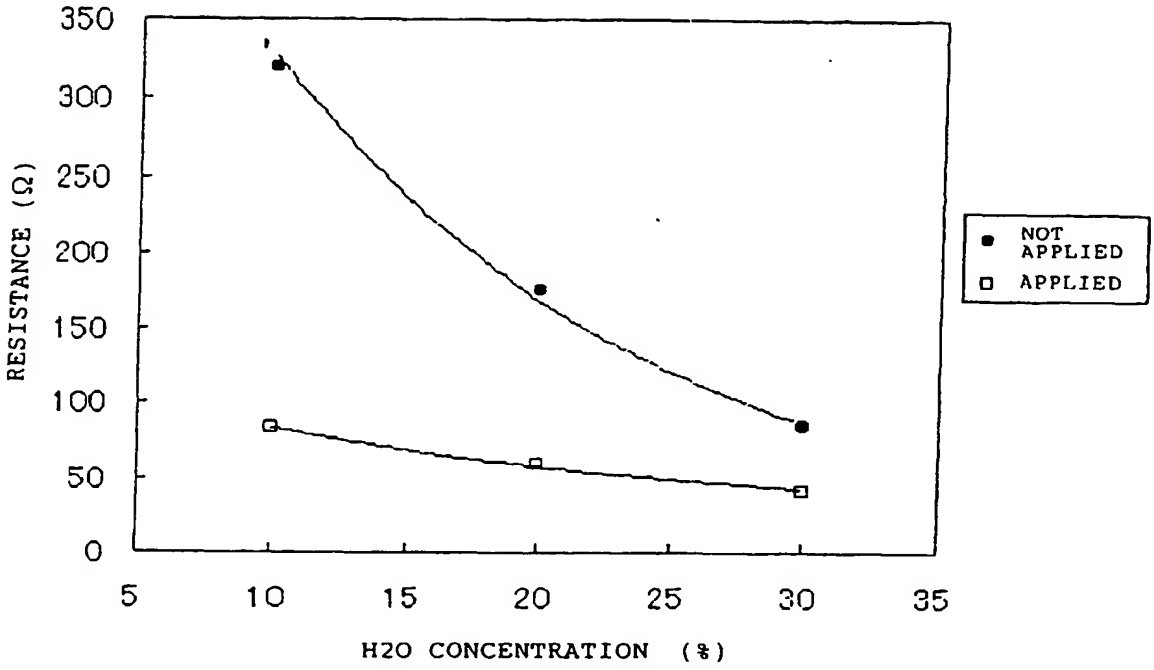

Fig. 8

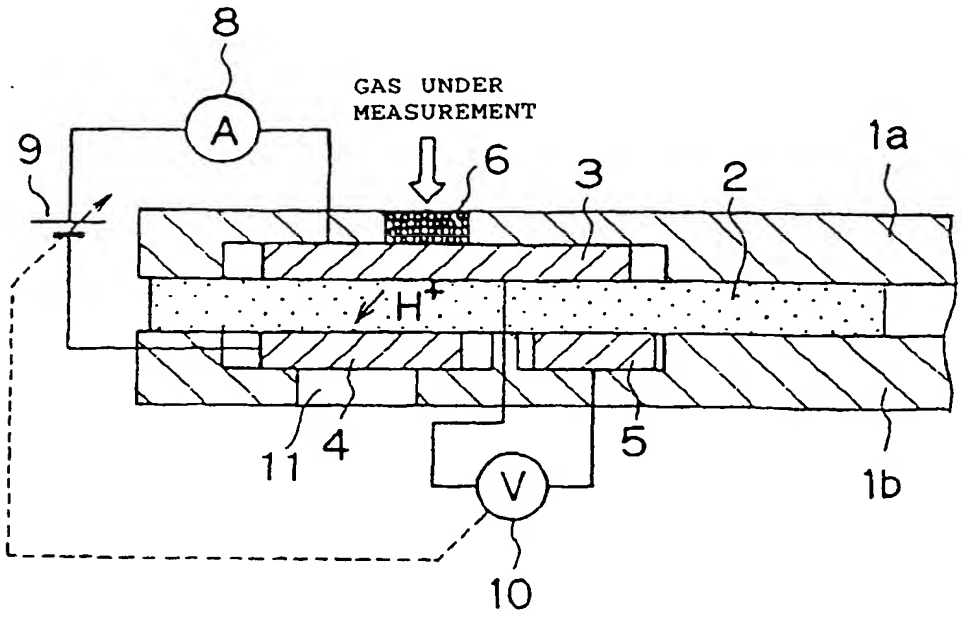

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Fig. 9

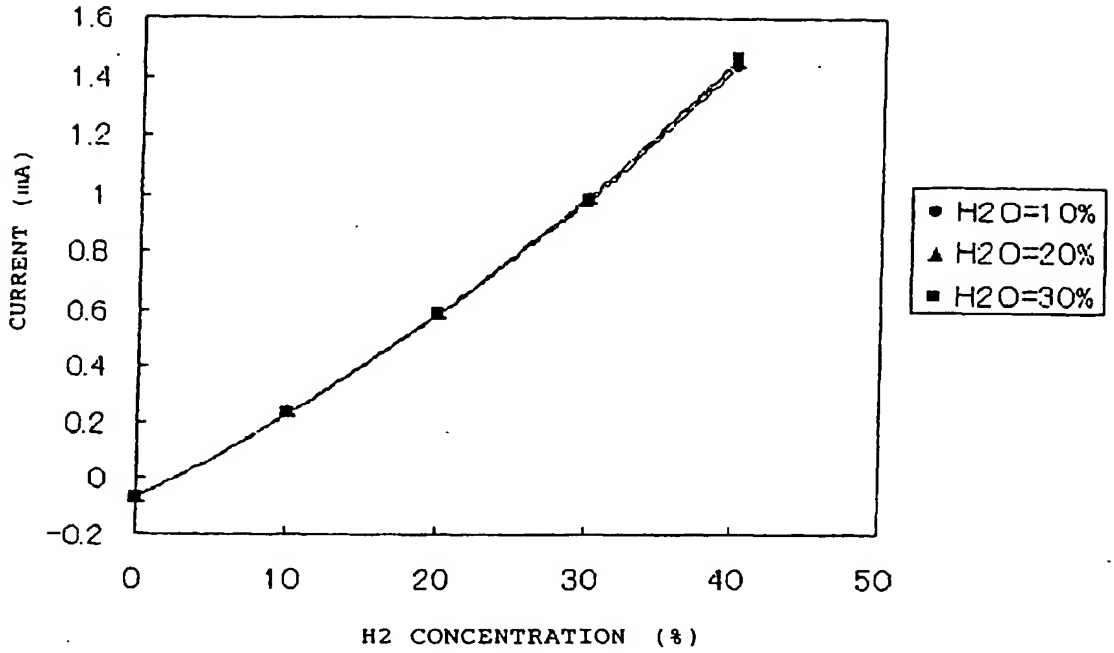

Fig. 10

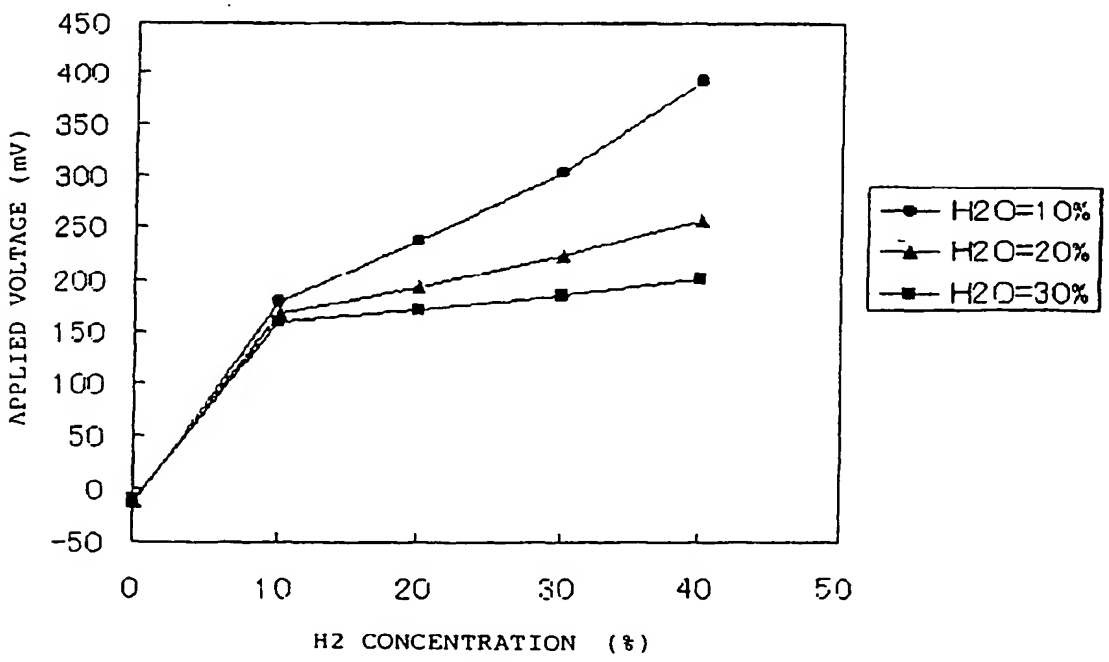

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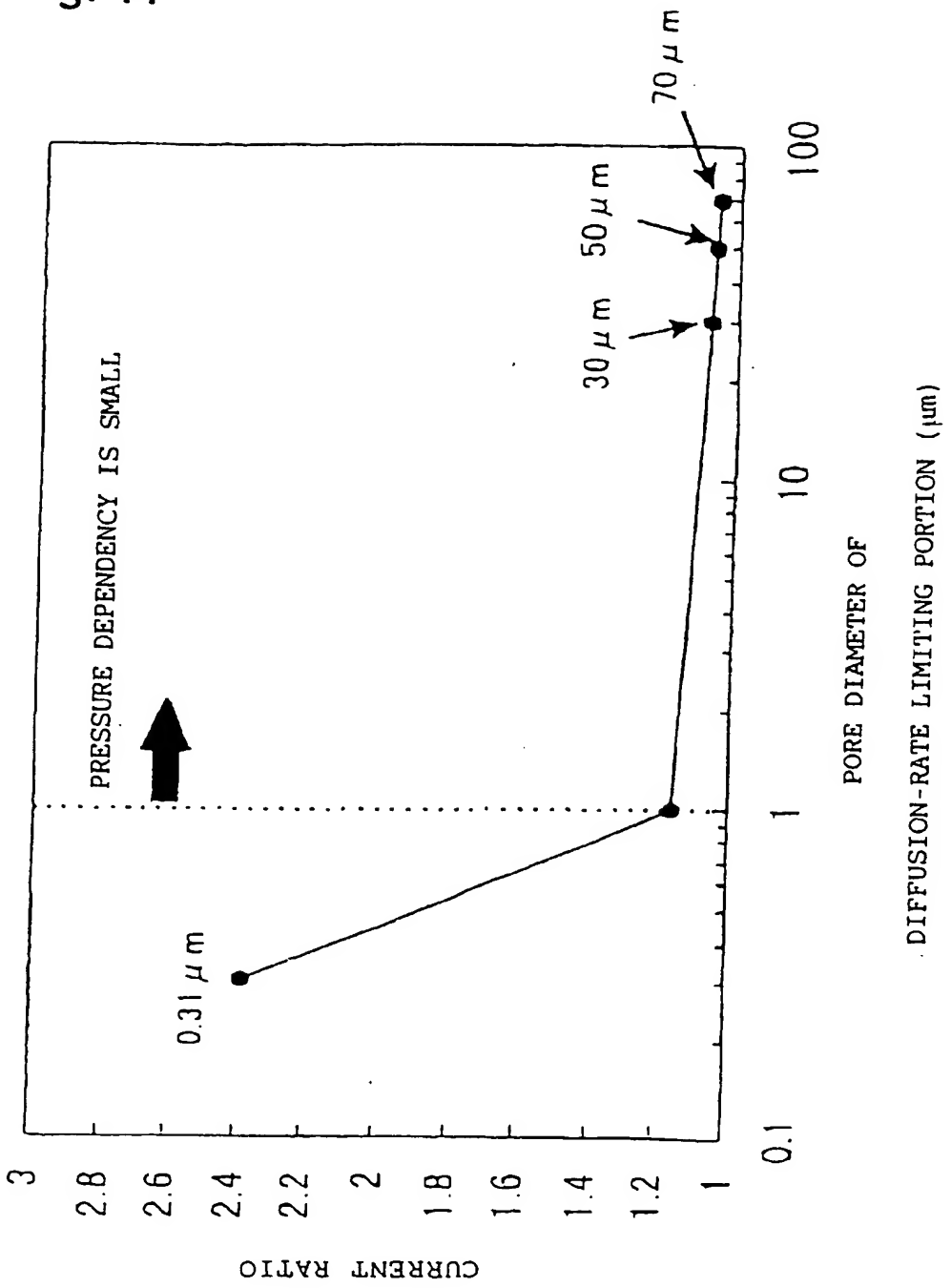
Fig. 11



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